Time-dependent, diffusion-controlled reactions: The influence of boundaries

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(Received 3 June 1988; accepted 21 September 1988)

A configurational averaging procedure is presented for the analysis of diffusion-controlled reactions in a medium containing a hard-sphere distribution of spherical sinks. The hierarchy of equations produced from the averaging procedure is truncated assuming low concentration of sinks. The method is shown to reproduce previous results for the decay of an initially uniform distribution of reactant in an unbounded medium and is subsequently applied to determine the reactant flux on the boundary of a semiinfinite domain. In the latter problem, the boundary has a significant effect which cannot be accounted for by the usual rate coefficient.

I. INTRODUCTION

The problem of interest is the reaction between a chemical species A with particles B located at fixed positions within a continuous phase which permits diffusion of A but is inert to chemical reaction. Such a situation is frequently encountered in problems such as the evaporation or condensation of sprays, growth of colloidal particles, suspension polymerization, and fluorescence quenching.[1,2] This problem was first studied by Smoluchowski[3] who considered the two-step process of slow diffusive transport followed by the rapid reaction of two chemical species. One of the species was assumed to be much more massive and was treated as a stationary, spherical sink.

Much of the recent work has focused on the steady problem where reactant is supplied by a uniform source or a distant boundary. Felderhof and Deutch sought an effective rate coefficient accounting for interactions between competing sinks at dilute sink volume fractions.[4] Muthukumar employed multiple scattering techniques to determine the rate coefficient[5] and diffusion coefficient[6] at arbitrary volume fractions of monopole sinks. More recently, Mattern and Felderhof[7,8] derived these coefficients by a cluster expansion approach and discussed discrepancies among previous results.

In the present work, we are concerned with the time-dependent problem. Felderhof determined a frequency-dependent rate coefficient and demonstrated the necessity for including "retardation" effects in the treatment of multisink interactions.[9] Bixon and Zwanzig[10] explored the transient problem employing a multiple scattering approach to derive a configurationally averaged Green's function to first order in sink density. Tokuyama and Cukier[11] employed a scaling expansion to derive a local damping equation in space and time. They showed that the reaction–diffusion process cannot be cast in conventional local form due to long-range spatial correlations for long times. Keizer studied the effect of chemical reaction rates using an analysis based on nonequilibrium pair correlation functions.[1] His approach has proven useful in a study of two-dimensional, diffusion-controlled reactions in membranes without the divergence difficulties encountered with the Smoluchowski theory.[12] Transient, one-dimensional systems have also attracted considerable attention since they permit simpler and more exact analysis.[13–16]

The unsteady problems analyzed in the above references involved infinite regions without boundaries. Boundaries introduce disturbances in the concentration field that cannot be fully accounted by conventional boundary conditions. This paper then has two objectives. One is to develop an alternative and, we believe, simpler analytical solution of the unsteady problem. The second is to extend the analysis to domains with boundaries. The analysis is based on configurational averaging initially formulated by Hinch[17] which we have previously applied to the steady problem.[18]

II. PROBLEM FORMULATION

The dimensionless equations which describe the reactant concentration in a domain Ω containing a suspension of perfect spherical sinks imbedded in an inert matrix material are

$$\nabla^2 U(\mathbf{x},t) - \frac{\partial}{\partial t} U(\mathbf{x},t) = 0 \tag{1}$$

for points in the matrix and

$$U(\mathbf{x},t) = 0 \tag{2}$$

for points lying within the spheres. These equations have been cast in dimensionless form using: $\mathbf{x} = \mathbf{x}'/a$, and $t = Dt'/a^2$ where a is the radius of the equisized spheres and D is the constant matrix diffusivity. In general, Eqs. (1) and (2) are solved subject to an initial distribution of reactant, $U(\mathbf{x},0) = U_i(\mathbf{x})$, and a prescribed boundary condition, $U(\mathbf{x},t) = G(\mathbf{x},t)$ for $\mathbf{x}$ on the boundary, $\partial\Omega$. Transforming the equations yields:

$$\nabla^2 u(\mathbf{x}) - su(\mathbf{x}) = -U_i(\mathbf{x}), \tag{3}$$

$$u(\mathbf{x}) = 0, \tag{4}$$

$$u(\mathbf{x}) = g(\mathbf{x}), \quad \mathbf{x} \in \partial\Omega, \tag{5}$$

where $u(\mathbf{x})$ and $g(\mathbf{x})$ are the Laplace transforms of $U(\mathbf{x},t)$ and $G(\mathbf{x},t)$; s is (dimensionless) frequency.

The spheres are distributed according to a hard-sphere potential with sphere center density n. The volume fraction of the spherical phase, $c = \frac{4}{3}\pi a^3 n$, is assumed small. Equations (3) and (4) are configurationally averaged to yield the infinite hierarchy of coupled equations[17,18]:

$$\nabla^2 u_0(\mathbf{x}) - s u_0(\mathbf{x}) = -(1-c)U_i(\mathbf{x}) + 3cB_1(\mathbf{x}), \qquad (6)$$

$$\nabla^2 u_1(\mathbf{x}) - s u_1(\mathbf{x}) = -(1-c)U_i(\mathbf{x}) + 3cB_2(\mathbf{x}) \quad \|\mathbf{x}-\mathbf{x}_1\| > 1, \qquad (7)$$

$$\nabla^2 u_2(\mathbf{x}) - s u_2(\mathbf{x}) = -(1-c)U_i(\mathbf{x}) + 3cB_3(\mathbf{x}) \quad \|\mathbf{x}-\mathbf{x}_1\|, \quad \|\mathbf{x}-\mathbf{x}_2\| > 1, \qquad (8)$$

where $u_N(\mathbf{x})$ is the configurationally averaged concentration field with sphere centers fixed at $\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3,\ldots,\mathbf{x}_N$. The factor $(1-c)$ reflects the absence of reactant within the sinks. The quantity $B_N(\mathbf{x})$ is defined by:

$$B_N = \frac{1}{4\pi}\int_{\{\|\mathbf{x}-\mathbf{x}_N\|=1\}\cap\Omega_{N-1}} \frac{\partial}{\partial n} u_N(\mathbf{x})\,d\mathbf{x}_N \qquad (9)$$

which is essentially the average rate of reactant consumption by a sink at $\mathbf{x}$ given sinks fixed at $\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3,\ldots,\mathbf{x}_{N-1}$. The restricted domain Ω_N is the allowed portion of the domain for sphere centers consisting of the domain Ω less the excluded hard-sphere volume in the neighborhood of the boundary, $\partial\Omega$, and N spheres fixed at $\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3,\ldots,\mathbf{x}_N$. All averaged equations are subject to boundary condition (5) on $\partial\Omega$ and Eq. (4) on all fixed sphere surfaces. Short-range correlations between the spheres which are induced by the hard-sphere potential[19] have been neglected throughout the foregoing averaging procedure which is valid for dilute volume fractions.[18] An effective rate coefficient can be defined

$$k u_0(\mathbf{x}) = B_1(\mathbf{x}) \qquad (10)$$

implying that the governing equation for the configurationally averaged concentration field may be cast in local form. This assumption is only valid far away from the domain boundary as discussed below.

The hierarchy must be truncated to permit solution of the unconditionally averaged field. The truncated hierarchy is solved in reverse order: the equation with the most spheres fixed is solved first because it is decoupled from the others; its solution provides the forcing term for the next equation. The procedure is continued until the unconditionally averaged field, u_0, is found.

The hierarchy is exploiting the assumption of diluteness ($c \ll 1$) and the physics of screening: far from a fixed sphere, its influence is "screened" by the presence of the intervening sinks in the material.[20] For large separation, $\|\mathbf{x}-\mathbf{x}_1\| \gg L_s$:

$$u_1(\mathbf{x}) \sim u_0(\mathbf{x}), \qquad (11)$$

where L_s is the "screening length" which is defined below. Using diluteness, $c \ll 1$, Eq. (7) is approximated by

$$\nabla^2 u_1(\mathbf{x}) - s u_1(\mathbf{x}) = -(1-c)U_i(\mathbf{x}) \qquad (12)$$

which is solved subject to boundary condition (4) and the screening relation (11) by elementary methods to obtain

$$B_1 = u_0(\mathbf{x}). \qquad (13)$$

Boundary condition (5) has been neglected in favor of Eq. (11). A $\sqrt{s}$ term is omitted from the above result based on Felderhof's argument[1] that its influence is negligible except for short times, $t' \approx a^2/D$. According to Eq. (10), the result is equivalent to Smoluchowski's solution[3]:

$$k_S = 1. \qquad (14)$$

Inserting Eq. (13) into Eq. (6) yields the "mean-field" truncation

$$\nabla^2 u_0(\mathbf{x}) - p u_0(\mathbf{x}) = -(1-c)U_i(\mathbf{x}), \qquad (15)$$

where $p = s + 3c$ is small for $t \gg 1$ and $c \ll 1$. By analogy to the foregoing procedure, higher-order truncations are obtained

$$\nabla^2 u_1(\mathbf{x}) - p u_1(\mathbf{x}) = -(1-c)U_i(\mathbf{x}), \qquad (16)$$

$$\nabla^2 u_2(\mathbf{x}) - p u_2(\mathbf{x}) = -(1-c)U_i(\mathbf{x}). \qquad (17)$$

Truncation (15) retains the screening effect of the spheres but neglects all direct sphere–sphere and sphere–boundary interactions. Truncation (16) retains sphere–boundary interactions and Eq. (17) includes two-sphere interactions. Rescaling Eqs. (15)–(17) to balance the diffusive and dissipative terms defines a screening length, $L_s = a|p^{-1/2}|$.

III. DECAY OF A UNIFORM DISTRIBUTION OF REACTANT

In this section, we consider the decay of an initially uniform distribution of reactant in an infinite medium of reactive spheres. Accordingly, $U_i(\mathbf{x}) = 1$, and u_0 and B_1 are spatially invariant.

We will truncate the hierarchy with Eq. (17) and use the commonly employed approximation[9]

$$B_2(\mathbf{x}) = \frac{1}{4\pi}\int_{\{\|\mathbf{x}-\mathbf{x}_2\|=1\}} \frac{\partial}{\partial n} u_2(\mathbf{x}_2)\,d\mathbf{x}_2, \quad \mathbf{x}\in\Omega_1$$
$$= 0, \quad x \notin \Omega_1. \qquad (18)$$

We can then write:

$$B_2(r) = B_1[1 - Q(r)], \quad r > 2$$
$$= 0, \quad r < 2, \qquad (19)$$

where $r = \|\mathbf{x}-\mathbf{x}_1\|$ and $Q(r)$ is the reduction in sink strength resulting from two-sphere interactions. Solving Eq. (17) and Eq. (4) up to two reflection disturbances yields[21]

$$Q(r) = \frac{e^{-\sqrt{p}r}}{r} - \frac{e^{-\sqrt{p}r}}{r^2}. \qquad (20)$$

Equation (7) becomes

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{du_1}{dr}\right) - s u_1 = -(1-c) + 3cB_1\left(1 - \frac{e^{-\sqrt{p}r}}{r} + \frac{e^{-\sqrt{p}r}}{r^2}\right), \quad r > 2$$
$$= -(1-c) \quad 1 < r < 2 \qquad (21)$$

which is solved for B_1:

$$B_1 = \frac{1-c}{s}\left\{1 + 3c\left[\frac{1}{s} - \frac{1}{\sqrt{s}+\sqrt{p}} - \ln(\sqrt{s}+\sqrt{p}) - \gamma_E - \ln 2\right]\right\}^{-1}, \qquad (22)$$

where $\gamma_E = 0.577\,22\cdots$ is Euler's constant and a term involving $\sqrt{s}$ has been neglected [cf. the remark following Eq. (13)]. Inserting this result into Eq. (6) yields

$$-su_0 = -(1-c) + 3c\frac{1-c}{s}\left\{1 + 3c\left[\frac{1}{s} + \frac{1}{\sqrt{s}+\sqrt{p}} + \ln(\sqrt{s}+\sqrt{p}) + \gamma_E + \ln 2\right]\right\}^{-1}. \quad (23)$$

Then, according to Eq. (10), we can express the solution in terms of an effective rate constant k

$$u_0 = \frac{1-c}{s+3ck} \quad (24)$$

given by:

$$k = \left\{1 - 3c\left[\frac{1}{\sqrt{s}+\sqrt{p}} + \ln(\sqrt{s}+\sqrt{p}) + \gamma_E + \ln 2\right]\right\}^{-1} + O(c^{3/2}\ln c) \quad (25)$$

which differs from Felderhof's solution[9]:

$$k_F = \left\{1 - 3c\left[\frac{1}{\sqrt{s}+\sqrt{p}} + \ln(\sqrt{s}+\sqrt{p}) + \gamma_E + \ln 3\right]\right\}^{-1} + O(c^{3/2}\ln c) \quad (26)$$

only in the order c term. The reason for the discrepancy is unclear. In the long-time ($s\to 0$) limit, these rate constants yield

$$k_\infty = 1 + \sqrt{3c} + \frac{3c}{2}\ln 3c + 3c(1 + \gamma_E + \ln 2), \quad (27)$$

$$k_{\infty,F} = 1 + \sqrt{3c} + \frac{3c}{2}\ln 3c + 3c(1 + \gamma_E + \ln 3), \quad (28)$$

both of which differ slightly from the steady-state rate constant determined previously by Felderhof and Deutch[4]

$$k_{\infty,FD} = 1 + \sqrt{3c} + \frac{3c}{2}\ln 3c + 3c(1 + \gamma_E + \ln 6), \quad (29)$$

where the dipole contribution has been omitted from their solution[4] for the sake of comparison. The steady-state rate constant has been determined by several others through a variety of techniques[1,5–8] and the different results discussed.[7] In the case of an initial uniform distribution of reactant, Bixon and Zwanzig's solution[10] reduces to

$$k_{BZ} = 1 + \sqrt{s} \quad (30)$$

which is obtained by neglecting two-sphere interactions ($Q = 0$) and retaining the $\sqrt{s}$ term in the solution of Eq. (21). At steady-state, $k_{\infty,BZ} = 1$ which coincides with Smoluchowski's solution.

The decay of an initially uniform distribution of reactant in an unbounded, dilue suspension of reactive spherical sinks is given by inversion of Eq. (24). The above solutions (with rate constants: k, k_F, k_{BZ}, and k_S) all decay exponentially for short times

$$U \sim U_F \sim U_{BZ} \sim U_S = (1-c)e^{-3ct}, \quad 3ct \ll 1 \quad (31)$$

but differ substantially in their long-time behavior. The Smoluchowski solution is given by Eq. (31) for all times which differs markedly from the long-time ($3ct \gg 1$) algebraic decay exhibited by the other solutions

$$U_{BZ} \sim \frac{1-c}{6c}\frac{1}{\sqrt{\pi t^3}}, \quad (32)$$

$$U = U_F \sim \frac{1-c}{6c}\frac{1-\sqrt{3c}}{\sqrt{\pi t^3}}. \quad (33)$$

This result implies that, at long times, the relative offset, $(U_F - U_{BZ})/U_F$, attains the value: $[-\sqrt{3c}/(1-\sqrt{3c})]$.

Figure 1 displays $U(t)$ for a sphere volume fraction of 0.01. The transition from exponential to algebraic decay is

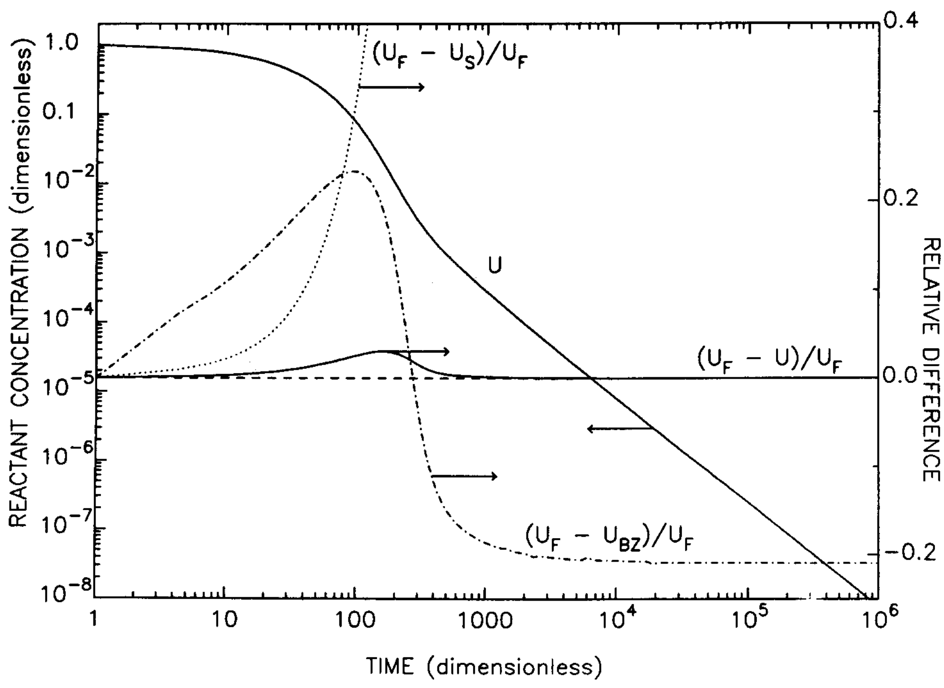

FIG. 1. Decay of an initially uniform distribution of reactant U with sphere volume fraction, $c = 0.01$ (–). Normalized differences between various solutions: $(U_F - U)/U_F$ (–); $(U_F - U_{BZ})/U_F$ (- · -); $(U_F - U_S)/U_F$ (· · ·).

apparent. The remaining curves show the difference between the above solutions and U_F. The difference between U_{BZ} and U_F results from neglecting two-sphere interactions thus demonstrating their significance. Initially, two-sphere interactions reduce the rate at which reactant is consumed thus, $U_F > U_{BZ}$ for short times. Two-sphere interactions appear to retard the transition from exponential to algebraic decay; during the transition, the relative difference between these two solutions changes sign and, at long times, $U_F < U_{BZ}$. Figure 1 predicts that the relative offset of the Bixon–Zwanzig solution is approximately -21% as quantitatively asserted by Eqs. (32) and (33). The relative difference between U_S and U_F diverges at $3ct \gtrsim 1$ thus marking the transition from exponential to algebraic decay in the solution derived herein as well as in the solutions of Felderhof and Bixon–Zwanzig. Figure 1 shows that the deviation of our solution (relative to U_F) is uniformly small ($\leqslant 3\%$) and tends to zero at both short and long times in agreement with Eqs. (31) and (33). Apparently, the present approach closely reproduces the results obtained by Felderhof.[9]

IV. REACTANT FLUX INTO A SEMIINFINITE DOMAIN

In this section, we determine the transient reactant flux on the boundary, $x = 0$ of a semiinfinite domain. We shall consider the case in which reactant concentration is initially absent from the domain $[U_i(\mathbf{x}) = 0]$. The boundary condition, $G(\mathbf{x},t)$, is assumed to be a slowly varying function of time and independent of position. Thus, the average concentration field u_0 and sink strength B_1 depend only on x, the distance normal to the boundary.

In the presence of boundaries, treating direct two-sphere interactions is very tedious, hence we shall truncate the hierarchy at an earlier stage, employing Eqs. (16) and (18)

$$B_1(x) = u_0(x)[1 + Q(x)], \quad x > 1,$$
$$B_1(x) = 0, \quad x < 1, \tag{34}$$

where $Q(x)$ is the sink strength enhancement induced by the boundary at $x = 0$. Solving Eq. (16) by the method of reflections[21] yields

$$Q(x) = \frac{e^{-2\sqrt{p}x}}{2x} + J(x;p), \tag{35}$$

where $J(x;p)$ is the contribution from the second and all higher-order reflections with the boundary. Equation (6) becomes

$$u_0''(x) - pu_0(x) = 3cu_0(x)\left[\frac{e^{-2\sqrt{p}x}}{2x} + J(x;p)\right], \quad x > 1,$$
$$u_0''(x) - su_0(x) = 0, \quad 0 < x < 1, \tag{36}$$

which must satisfy Eq. (5) and is solved by the following perturbation scheme for $|p| \ll 1$ which implies diluteness since $c \leqslant |p|$. Introducing the scaled independent variable, $\tilde{x} = x\sqrt{p}$, Eq. (36) becomes

$$u''(\tilde{x}) - u(\tilde{x}) = \frac{3c}{\sqrt{p}}u(\tilde{x})\left[\frac{e^{-2\tilde{x}}}{2\tilde{x}} + O\left(\frac{\sqrt{p}}{\tilde{x}^2}\right)\right], \quad \tilde{x} > \sqrt{p},$$
$$u''(\tilde{x}) - \frac{s}{p}u(\tilde{x}) = 0, \quad 0 < \tilde{x} < \sqrt{p}, \tag{37}$$

where the subscript, 0, indicating unconditional average has been dropped and is heretofore implied. Deriving the first two terms in a regular perturbation yields the uniformly valid approximation

$$u(x) = ge^{-\sqrt{p}x}\left\{1 + \frac{3c}{4\sqrt{p}}\left[E_1(2\sqrt{p}x) - e^{2\sqrt{p}x}E_1(4\sqrt{p}x) - \ln 2\right] + O(c)\right\}, \tag{38}$$

where $E_1(x)$ is the exponential integral. Then, assuming that $G(t)$ attains a constant steady-state value, G_∞, the steady-state $(s \to 0)$ concentration field is

$$U_\infty(x) = G_\infty e^{-\sqrt{3c}x}\left\{1 + \frac{\sqrt{3c}}{4}\left[E_1(2\sqrt{3c}x) - e^{2\sqrt{3c}x}E_1(4\sqrt{3c}x) - \ln 2\right] + O(c)\right\} \tag{39}$$

which, far from the boundary, relaxes to

$$U_\infty(x) = G_\infty e^{-\sqrt{3c}x}\left[1 - \frac{\sqrt{3c}}{4}\ln 2\right], \quad \sqrt{3c}x \gg 1. \tag{40}$$

The reactant flux on the boundary is obtained by differentiation of Eq. (38)

$$\begin{aligned} f &= -\left.\frac{du}{dx}\right|_{x=0} \\ &= g\left\{\sqrt{p} + \frac{3c}{4}\left[E_1(2\sqrt{p}) + E_1(4\sqrt{p}) - \ln 2\right] + O(c)\right\} \\ &= g\left[\sqrt{p} - \frac{3c}{4}\ln p - 3c\left(\ln 2 + \frac{1}{2}\gamma\right) + O(c)\right]. \end{aligned} \tag{41}$$

The result given by Eq. (41) is accurate to order $c \ln c$ but can be refined to $O(c)$ by manipulating Eq. (36) to yield the implicit relation

$$f = g\sqrt{p} + 3c\int_1^\infty e^{-\sqrt{p}x}u(x)\left[\frac{e^{-2\sqrt{p}x}}{2x} + J(x;p)\right]dx. \tag{42}$$

When the first term of Eq. (38) is inserted into the integral of Eq. (42), the following result is obtained

$$f = g\left\{\sqrt{p} + \frac{3c}{4}\left[E_1(2\sqrt{p}) + E_1(4\sqrt{p}) - \ln 2\right] + 3cj + O(c^{3/2}\ln c)\right\} \tag{43}$$

which produces the $O(c \ln c)$ solution and an additional term, $g(3cj)$, resulting from the contribution of higher-order reflections with the boundary. $J(x;p)$ is continuous and bounded uniformly by $O(x^{-2})$ as $x \to \infty$. Therefore, the improper integral of J on $[1, \infty)$ converges uniformly in p as $p \to 0$ which permits the limiting process

$$j = \frac{1}{g} \lim_{p \to 0} \int_1^\infty e^{-\sqrt{p}x} u(x) J(x;p) dx$$
$$= \int_1^\infty J(x;0) dx = 0.474\,72\cdots. \tag{44}$$

The quantity $J(x,0)$ is known exactly from the solution of Laplace's equation in bispherical coordinates[22] and the integration is performed numerically. In the low-frequency limit $(s \to 0)$, Eq. (43) reduces to

$$F_\infty = G_\infty \left[\sqrt{3c} - \frac{3c}{4} \ln 3c - 3c \left(\ln 2 + \frac{1}{2}\gamma - j \right) + O(c^{3/2} \ln c) \right] \tag{45}$$

which nearly reproduces the recently obtained steady-state solution of Loewenberg and Gavalas[18]

$$F_{\infty,LG} = G_\infty \left[\sqrt{3c} - \frac{3c}{4} \ln 3c - 3c \left(\frac{3}{4} \ln 3 + \frac{1}{2}\gamma - j \right) + O(c^{3/2} \ln c) \right]. \tag{46}$$

The discrepancy between expressions (45) and (46) is similar to that found between k and k_F and cannot be readily explained. In deriving the steady-state result, Loewenberg and Gavalas demonstrated that two-sphere interactions affect the solution at $O(c^{3/2} \ln c)$, a result assumed to hold in the present, time-dependent situation for $3ct \gg 1$. For short times, two-sphere interactions have a smaller, order c^2 effect. Thus, in the context of this problem, the omitted two-sphere interactions have a uniformly higher-order effect than the sphere–boundary interactions which are treated above.

According to Eqs. (10) and (34) we can identify a rate coefficient

$$k(x) = 1 + \frac{e^{-2\sqrt{p}x}}{2x} + J(x;p), \quad x > 1$$
$$= 0, \quad x < 1 \tag{47}$$

which is specific to the boundary considered in this problem indicating that the bulk equations depend on the choice of boundary. Therefore, application of an effective rate coefficient which treats two-sphere interactions and is derived for the boundary–free problem would be inconsistent. A comparison of this result with Eq. (14) indicates that the rate coefficient describing the average concentration field deviates from that for an infinite domain inversely with distance from the boundary.

To assess the significance of sphere–boundary interactions, the above results are compared with the Smoluchowski solution which neglects all interactions except screening. The quantities u_S and f_S are obtained by solving Eq. (15)

$$u_S = g e^{-\sqrt{p}\,x}; \quad f_S = g\sqrt{p} \tag{48}$$

which at steady-state, reduce to

$$U_{\infty,S} = G_\infty\, e^{-\sqrt{3c}x}; \quad F_{\infty,S} = G_\infty \sqrt{3c}. \tag{49}$$

Equations (41) and (48) indicate that sphere–boundary interactions affect the reactant flux at order $c \ln c$. A comparison of Eqs. (40) and (49) indicates that the relative far-field $(\sqrt{3c}\,x \gg 1)$ depletion at steady state which results from sphere–boundary interactions is $O(\sqrt{c})$.

As an illustration, we shall consider the transient reactant flux resulting from a unit step change in reactant concentration with sphere volume fraction, $c = 0.01$. Thus, $G(t)$ is given by the Heaviside function which has the transform, $g = 1/s$, and the steady-state value, $G_\infty = 1$. For short times, the solution is dominated by sink-independent algebraic decay

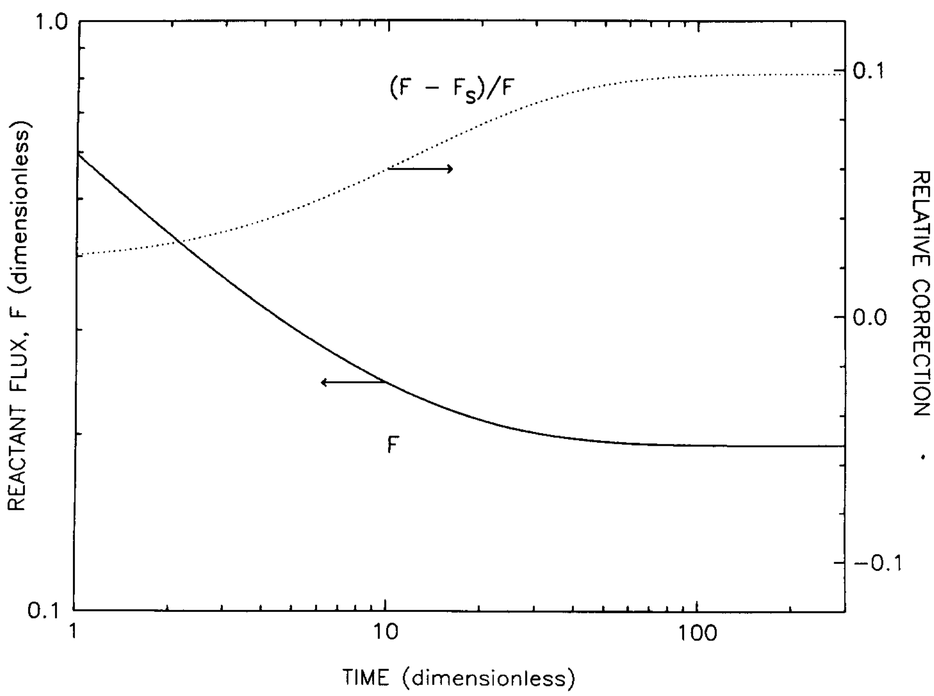

FIG. 2. Reactant flux F into a semiinfinite medium resulting from a step change in the boundary concentration with sphere volume fraction, $c = 0.01$ (–). The relative effect of sphere–boundary interactions: $(F - F_S)/F$ (· · ·).

$$F \sim \frac{1}{\sqrt{\pi t}}, \quad 3ct \ll 1 \tag{50}$$

and attains the steady value, F_∞, at $3ct \approx O(1)$ as shown in Fig. 2. The remaining curve shows $(F - F_S)/F$ and demonstrates that sphere–boundary interactions enhance the reaction flux and become most significant at long times. According to Eqs. (40) and (49), the sphere–boundary interactions deplete the steady-state far-field concentration by about 3%, but enhance the steady-state reactant flux by approximately 10% as indicated in Fig. 2. For the parameters used in this example, the steady-state flux, F_∞, deviates from the previous result, $F_{\infty,LG}$, by about 2%.

V. CONCLUSIONS

A configurational averaging approach was developed to analyze diffusion-controlled reactions. This approach reproduces previous results for the case of an unbounded medium. The calculated reactant concentration exhibits exponential decay initially and slow $t^{-3/2}$ decay for $3ct \gg 1$. Two-sphere interactions were included and their effect shown to be order $\sqrt{c}$ for long times. The configurational averging technique was then used to determine the time-dependent reactant flux in a medium with a macroscopic boundary. The presence of the boundary affects the averaged equations which govern the bulk concentration field. Thus, an effective rate coefficient cannot be consistently applied. The analysis shows that the boundary induces an order $c \ln c$ enhancement of the reactant flux and an order $\sqrt{c}$ depletion to the steady-state far field. An illustration shows that although the effect of sphere–boundary interactions on the far field is small, the effect on the reactant flux on the boundary is more significant. This flux algebraically approaches a steady-state value in close agreement with a previous result. In general, it appears that the configurational averaging approach is simpler than previous approaches and is well suited to treat bounded domains.

ACKNOWLEDGMENT

This work was made possible through a fellowship from the LINK foundation.

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